

SOME PHOTOACTIVE PROPERTIES
of
METALS IN ELECTROLYTIC CELLS.

by

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A THESIS SUBMITTED TO THE DEPARTMENT OF PHYSICS
AND THE FACULTY OF THE GRADUATE SCHOOL OF THE
UNIVERSITY OF KANSAS IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS.

Approved by:



Department of Physics

OUTLINE.

I. Introduction.

A. Theoretical Aspect.

a. Work of Einstein.

B. Experiments of Millikan.

C. Experiments of Early Investigators.

a. Becquerel.

b. Minchin.

c. Hertz, Elster and Geitel.

d. Murdock.

e. Goldschmitt.

II. Body.

A. Statement of Present Problem -- to find out, if possible, the existence of potentials in metals illuminated by light, in water.

B. Methods of Attack.

a. Measurement of Current with a Galvanometer.

1. Use of Copper Cell -- Results.

2. Use of Cell with Platinum Electrodes.

b. Use of Electrometer.

1. Direct Illumination.

2. Measurements of Potential on Cell with Platinum Electrodes.

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SOME PHOTOACTIVE PROPERTIES OF METALS IN ELECTROLYTIC CELLS.

The problem of photo activity of metals has received much attention in the past few years. According to the theory developed by Einstein, an emission of electrons from metals under the action of light should occur. This would charge the metal positively.

In his development of the formula, Einstein assumes that light is discontinuous in its distribution thru space, and its emission and absorption is a discontinuous process. In other words, light is composed of finite bundles of energy. The formula

$$1/2 mV^2 = \text{Kinetic Energy} = Ve = h\nu - w$$

represents a straight line relation between frequency of incident light and electrical potential impressed. V is the electrical potential, e the value of the elementary charge of electricity, h is planks constant, ν the frequency of light, and w the amount of work required to drive the electron out of the metal. The intercept of this straight line on the frequency axis will give the lowest frequency that will produce photoelectrical effect.

Experimental research in recent years, especially that of R. A. Millikan, has fairly conclusively proved the validity of the foregoing equation. These experiments give good results of planks constant h .

Hertz found that a spark would pass more easily between electrodes when illuminated, than when dark. Various experimenters have investigated this effect, chiefly Elster and Geitel. However, the true photoelectric phenomenon is complicated by the conduction thru the air of gaseous ions, and by the formation of films on the surface of the metal.

Becquerel performed some experiments in which the illuminated and dark electrodes were in solutions. Plates coated with silver, over which a coating of a silver salt was deposited, were used. He found that when a thin layer of salt was present, the illuminated electrode was positive under the action of light, while the reverse was true if a thicker layer was used. The action of the violet light was twenty-two times that for the red.

Minchin made measurements of photo active cells, consisting of glass plates coated with tinfoil. The surface of the tinfoil was coated with a photographic emulsion. He found a much greater effect in the blue than any other part of the spectrum. He experimented with many types of cells, some being treated, others not. He obtained different values of electrical potential for different methods of treatment of the surface.

The following criticisms might be made of his work:

He did not take precautions to have the part of his active electrode which was not illuminated, insulated from the solution.

In most cases, the materials used gave ample opportunity for photochemical effects to occur.

He seemed to be working with a practical end in view --- to perfect a light sensitive cell. He showed little as to the real nature of photoactivity.

Other investigators have experimented with photoactive cells of a similar nature, such as Goldmann, Nichols and Merritt, Hodge, and Murdock. These experimenters on the most part used organic dyes in their solutions, and attempted to find some relation between fluorescence and photo activity.

When fluorescent substances are used, there is a gradual rise of current with time, while the true photoelectric effect is instantaneous. This tends to show that there are other factors than direct emission of electrons from the illuminated electrode when in fluorescent solutions.

The problem which is the subject of this investigation is to determine the effect of a material of high dielectric constant on photoelectric emission. Less work should be required to expel the electrons from the metal, and hence a lower frequency of light would produce measurable photoelectric activity, if some material such as water covered the metal during illumination.

Preliminary investigation was begun with current measurement. A Leeds Northrup galvanometer of 2290 megohm sensitivity was

used. A cell was made by scraping a bare spot on one side of a piece of Oakenite wire. The insulation stuck very securely to the copper, and there was little danger of liquid coming in contact with unilluminated portions of the wire. A porous-cup was placed over the dark electrode. Thus current effects between the illuminated and dark electrode could be measured. For wiring diagram see Figure 1.

The first difficulty encountered was that of what has been termed "dark current". In the copper sulphate solution, or even in distilled water, a current flowed between the two copper terminals, and was of a value larger than could be measured by the galvanometer without the use of a shunt.

In order to evade this difficulty, a potentiometer scheme was tried. However, it was found that the potential, and consequently the zero point on the galvanometer, varied in a very erratic manner. There was also a gradual decay of the potential due to polarization, when potentiometer potential was applied.

Then a series of copper -- copper sulphate -- copper cells was made, the polarity of each tested, and put in opposition to each other. It was hoped that the chance variations of each cell would produce a resultant effect that would be nearly zero. It was not entirely satisfactory, yet some measurements were made.

A 500 watt Tungsten lamp was used at first as a source of

light. The average deflection obtained was 5 cms. Different pieces of wire were used, and in every case the illuminated electrode was positive. An iron arc with tapered iron points was then used as a source of light. A metallic concave mirror concentrated the light from the carbon vapor on the bare copper wire. A deflection of 30 centimeters was obtained. When the light from the crater was focused on the wire, a smaller deflection was obtained, though the illumination was ^{more} less intense.

A flat glass flask of walls about 3 mm in thickness was interposed. The average of several trials showed about 40 percent reduction of deflection. When water was put into the flask, making a path three centimeters, the average reduction of deflection was 47 percent.

The cell did not remain in its most sensitive condition, but would die down with exposure. However, this may have been due to unsteady illumination.

Several causes may be attributed to the phenomena observed:

1. Thermal effects.
2. Photochemical effects.
3. True photoelectric emission.

That the effect was not entirely due to heating of the electrode by illumination was shown by the fact that ultra-violet from the open

arc had such a strong influence on the magnitude of the deflections. Photochemical actions might take place, or some intermediate energy change than directly from light to electrical energy. This is shown in the experiments of Murdock and Goldmann. Whether the true photoelectric effect is present or not is much open to question.

Then a new type of cell was constructed (see Figure 2). A rectangular disc of platinum, to which a platinum wire had been welded, was sealed into a flat bead of glass, and ground till a flat surface of twenty-five millimeters in dimensions was exposed. Care was taken in polishing that the edge between platinum and glass contained no pits or crevices, so that liquid could come in contact with an unilluminated portion of the electrode. To the flat surface containing the sealed-in platinum plate was cemented a short piece of glass tubing with a T joint in the side, as shown in the diagram. At the bottom of the T joint was a small platinum wire seal, which served as the dark electrode. The outside of the T joint was wrapped with tape to prevent the light from penetrating to the dark wire.

Distilled water was put into the cell, and a galvanometer connected to the electrodes. The dark currents before observed were not present here. A potentiometer was used and potentials impressed on the all. Due to polarization, the equivalent of a consenser was formed. The cell was charged and discharged thru a galvanometer.

The current values for charge and discharge were taken for .1 volt and .3 volt, the illuminated electrode being positive and negative in turn. Both electrodes were kept dark, and the values compared with the value when one was illuminated. No difference could be measured, above that of experimental error.

The quantity of electricity in discharge was found to be greater when the larger electrode was negative than when it was positive. This may be because the water, ionized into O and $2H^+$ forms a larger capacity when the larger electrode is negative than positive, since there are twice as many positive as negative ions.

The data shows that for a potential of .1 volt, after a given time there is a stopping of the current when the cell is being charged. At .3 volt, a small current continued to flow after the potential had been built up.

Studies of Polarization.

A solution of silver nitrate into which two glass plates coated with silver constituted a cell which was studied. Two volts was applied to the cell, and the current read with a shunted galvanometer. The galvanometer was critically damped and current curves for charge and discharge were taken. It was found that gaseous ions were deposited on the electrodes as well as the transfer of silver that took place.

When the silver plates were first immersed in the silver nitrate, and connected to a galvanometer, the same dark currents were observed as in the copper-copper sulphate cell. If a potential were applied in either direction, however, a gaseous cell was formed which on discharge showed a complete lack of the "dark currents".

Again, potentials were impressed on the cell in alternate directions, and on discharge, showed an alternating current, for a few oscillations took place showing that ions were deposited in layers.

The Use of the Capillary Electrometer.

The capillary electrometer consists of a small capillary tube (see Figure 3) containing mercury in contact with a solution of sulphuric acid. As shown in the figure, contact on one side is made with the mercury thru a platinum wire sealed into a glass tube, and on the other side by a similar glass rod in contact with mercury, which in turn presents a large surface in contact with sulphuric acid solution.

Due to the surface tension of mercury, the column will not rise as high in the capillary tube as in the tube of larger diameter, the smaller the diameter of the capillary, the greater the depression. When a voltage is applied to the terminals, according to the Helmholtz theory, a double layer is formed, and the surface tension will be

changed due to mutual repulsion of the charges. Measurements of capacity were made, and it was found to be 3 m.f. for the capillary electrometer used.

The curves of potential v.s. depressions of mercury column, which is proportional to surface tension, show that the mercury is already positively charged with respect to the solution. As a negative potential is applied to the electrometer, the surface tension increases, as the column becomes more depressed in the capillary, reaches a maximum at about .9 volt, and then begins to decrease.

Several calibration curves were made with different concentrations of acid. At first, distilled water was used, but the sensitivity was very small. The calibration curve shown was with 1-10 parts by volume of sulphuric acid and water.

It was found that the calibration curve was not constant for the same concentration, varying with the amount of time of impressed voltage.

It was also found that the solution came in contact with the capillary of mercury not only at the top curvature, but all the way down the mercury column. This could be shown by the fact that when overvoltage was applied, bubbles of gas formed all along the mercury.

It was hoped that by shining the light on the mercury column, if there was any potential produced by light on the mercury capillary, the instrument would register it.

A mirror was placed back of the capillary tube, in order that all sides of the mercury might be illuminated. The glass capillary acted as a cylindrical lens, focusing the rays from the arc on the mercury. Violet light from the vapor of an iron-carbon arc was used, focused by means of a concave metallic mirror.

The electrometer was charged with a potentiometer positively to .01 volt, and discharged by a key thru a galvanometer, and the deflection noted. Then the capillary was illuminated, and the deflection again observed. It was greater when illuminated by an average of 1.3 centimeters deflection. There was a steady decay of the photo-activity as nearly as could be judged from the data.

The electrometer was allowed to remain in open circuit, and it was found that a positive charge accumulated on the mercury, which would disappear when the two electrodes were connected together. When illuminated, the rate of accumulation of charge was decidedly more rapid than dark. Light from the arc was allowed to pass thru a narrow slit to the capillary, and flashed on and screened alternately, and the effect was very evident. Then wratten filter number 26, allowing red light to fall on the mercury, was placed in the path of the beam.

The graphs show accumulation of positive charge. A certain definite constant value was reached, and then a violet screen replaced the red one. A larger potential accumulated on the mercury. When the screen was removed, some of the charge disappeared.

The experiment was repeated with a saturated solution of mercurous sulphate in the sulphuric acid, but no effect was observed in this case.

Then the platinum electrodes of the cell of Figure 2 were electroplated with copper. An electrometer was connected to the terminals and the effect of light on the electrode when immersed in a copper sulphate solution was studied, this time potentials instead of current were measured.

There was a potential of negative value present on the illuminated electrode, of constantly changing magnitude. On illumination a small potential of the value .00025 volt was produced, this time the illuminated electrode became negative.

The capillary electrometer was provided with a lead screen, having a narrow slot the width of the capillary tube. It was caged to prevent electrostatic effects, and put in the path of the rays from a Coolidge tube. No conclusive results were observed.

The following conclusions may be drawn from the foregoing experiments:

1. There is a small voltage produced on metals by the action of light, which is greater for violet than for red.
2. These voltages are very small as compared with photoelectric voltages.
3. Ionization effects produce a double layer at the surface of the metal, which might prevent the water from coming in contact with it.

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DEFLECTIONS OF GALVANOMETER IN CENTIMETERS SHOWING SEVERAL
OSCILLATIONS.

Illuminated plate charged positively with .1 volt.

<u>Cell Illuminated</u>				<u>Cell Dark</u>			
<u>Charge</u>		<u>Discharge</u>		<u>Charge</u>		<u>Discharge</u>	
	:		:		:		:
4	:	44	:	4.15	:	3.7	:
2.8	:	3.5	3.2	2.9	3.05	2.7	2.7
	:		:		:		:
2.9	:	2.6	2.55	2.4	2.4	2.2	2.2
	:		:		:		:
2.3	:		:		:		:
	:		:		:		:
2.3	:		:	4.7	:	4.75	:
	:		:		:		:
	:		:	3.3	3.5	3.35	3.35
	:		:		:		:
	:		:	2.8	2.7	2.7	2.8

CELL CHARGED WITH ILLUMINATED PLATE

.1 VOLT NEGATIVE.

<u>Illuminated</u>				<u>Dark</u>			
<u>Charge</u>		<u>Discharge</u>		<u>Charge</u>		<u>Discharge</u>	
	6.5		6.5	:	6.3		6.7
4.4		4.5	4.7	:	4.2	4.2	4.4
3.6	4.9	3.7	3.7	:	3.4	3.7	3.7

.3 VOLT NEGATIVE.

<u>Illuminated</u>				<u>Dark</u>			
		21.5		:			22.3
12.0		14.8		:	13.0		15.2
10.0		11.5		:	11.0		11.9
8.1		8.3		:	8.8		9.2
6.3		7.4		:	7.0		7.5
5.0		6.0		:	5.5		6.1
3.9		4.9		:	4.3		4.7
2.3		3.3		:	3.3		4.0
2.7		2.7		:	2.7		3.3
1.3		2.3		:	2.05		2.7
1.0		1.9		:	1.5		2.2

DISCHARGE OF CAPILLARY ELECTROMETER THRU GALVANOMETER.

DEFLECTIONS IN CENTIMETERS OF SEVERAL OSCILLATIONS.

Mercury column charged positively .01 volt.

<u>Illuminated</u>		<u>Dark</u>	
22.3	: 13.5	20.	: 12.2
:	:	:	:
13.6	: 9.15	13	: 9.60
:	:	:	:
<u>9.45</u>	<u>: 6.25</u>	<u>9</u>	<u>: 5.95</u>
:	:	:	:
22.5	: 13.15	21.4	: 13.2
:	:	:	:
13.8	: 9	13.85	: 9.25
:	:	:	:
<u>9.55</u>	<u>: 6.15</u>	<u>9.60</u>	<u>: 6.35</u>
:	:	:	:
21	: 12.65	21.2	: 12.6
:	:	:	:
13.55	: 8.95	13.65	: 9
:	:	:	:
<u>9.35</u>	<u>: 6.10</u>	<u>9.5</u>	<u>: 5.15</u>
:	:	:	:
20.9	: 12.7	20	: 11.8
:	:	:	:
13.4	: 9	12.9	: 8.3
:	:	:	:
<u>9.2</u>	<u>: 6.15</u>	<u>9</u>	<u>: 5.7</u>
		:	:
		20.2	: 12.6
		:	:
		13.8	: 9
		:	:
		<u>9.2</u>	<u>: 6.15</u>

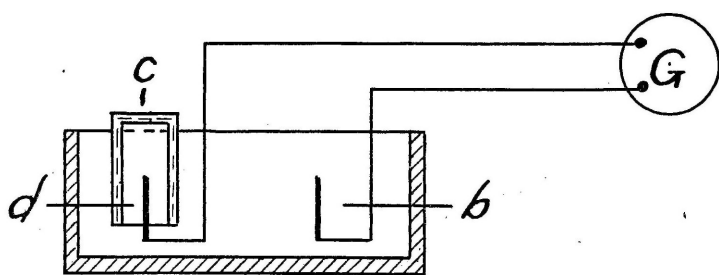


Fig. 1. Photo electric cell.

c. Porous cup.

d. Dark electrode.

b. Illuminated electrode.

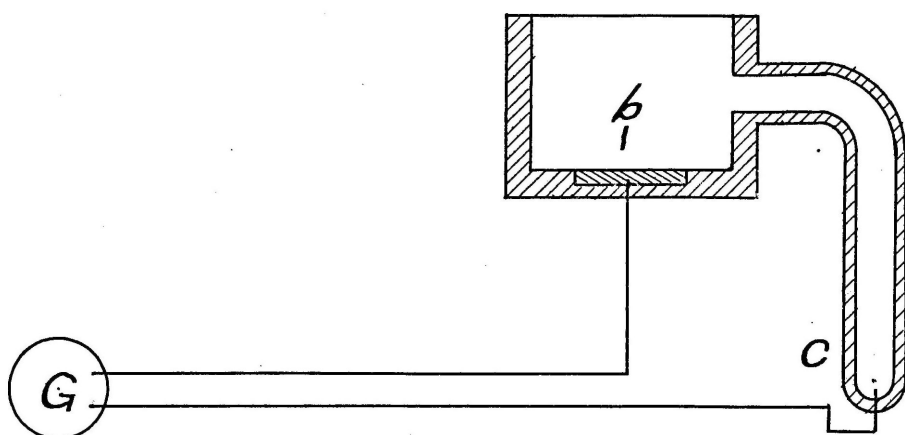


Fig. 2. Photo electric cell.

b. Illuminated platinum electrode.

c. Dark electrode.

G. Galvanometer.

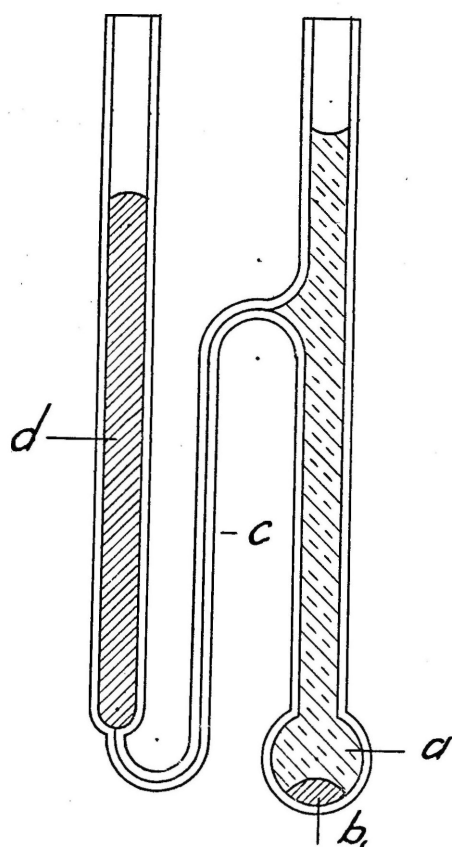
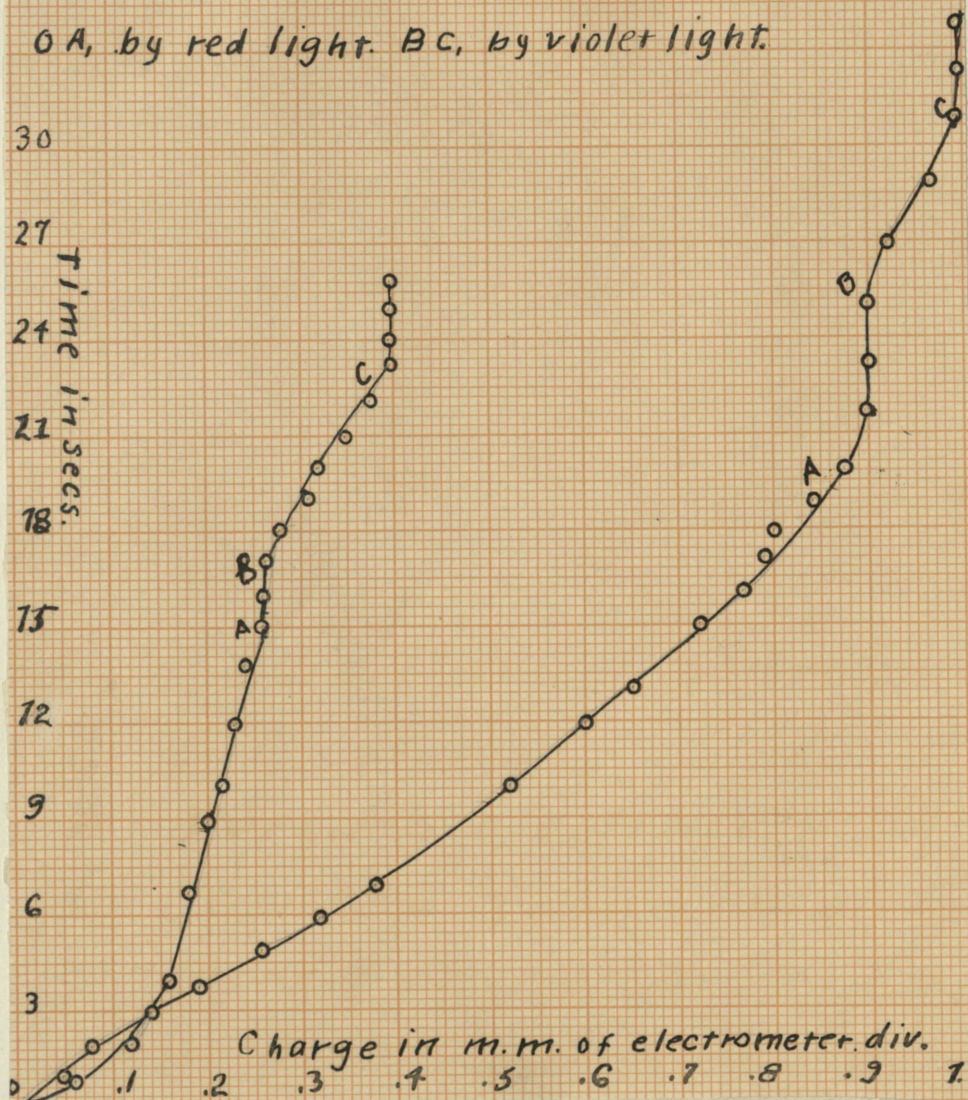


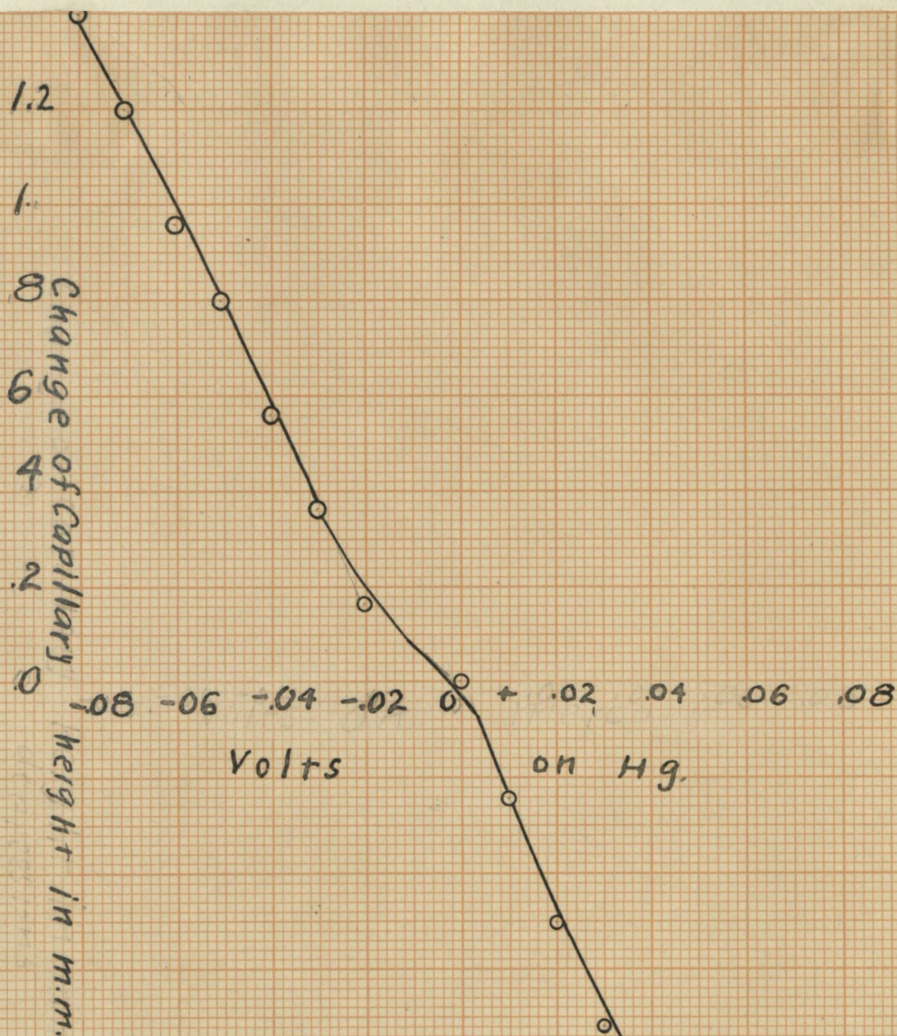
Fig. 3. Capillary Electrometer.

- a. Bulb containing sulphuric acid.*
- b. Mercury electrode.*
- c. Capillary tube containing a thread of mercury in contact with the sulphuric acid.*
- d. Mercury column.*

Curves showing accumulation of positive charge of illuminated electrometer.

OA, by red light. BC, by violet light.





Calibration Curve
of
Capillary Electrometer

